

# Electronic structure of BaCu<sub>2</sub>As<sub>2</sub> and SrCu<sub>2</sub>As<sub>2</sub>: sp-band metals

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The electronic structures of ThCr<sub>2</sub>Si<sub>2</sub> structure BaCu<sub>2</sub>As<sub>2</sub> and SrCu<sub>2</sub>As<sub>2</sub> are investigated using density functional calculations. The Cu *d* orbitals are located at 3 eV and higher binding energy, and are therefore chemically inert with little contribution near the Fermi energy. These materials are moderate density of states, sp-band metals with large Fermi surfaces and low anisotropy.

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Recent results, motivated by the discovery of high temperature Fe-based superconductivity,<sup>1</sup> have shown that 3*d* pnictides in the ThCr<sub>2</sub>Si<sub>2</sub> structure show a remarkable range of properties. This includes the itinerant spin density wave and high temperature superconductivity characteristic of the Fe-based superconductors for BaFe<sub>2</sub>As<sub>2</sub>, SrFe<sub>2</sub>As<sub>2</sub> and CaFe<sub>2</sub>As<sub>2</sub>.<sup>2,3,4,5,6,7</sup> Remarkably, in contrast to cuprates, superconductivity can be induced by doping on the Fe-site, using Co and Ni as electron dopants.<sup>8,9</sup> BaCo<sub>2</sub>As<sub>2</sub> and BaNi<sub>2</sub>As<sub>2</sub>, show very different properties, namely those of a material very close to ferromagnetism,<sup>10</sup> and a low temperature electron-phonon superconductor, respectively.<sup>11,12,13</sup>

The electronic structures of BaFe<sub>2</sub>As<sub>2</sub>, BaCo<sub>2</sub>As<sub>2</sub> and BaNi<sub>2</sub>As<sub>2</sub> are, however, closely related,<sup>10,13,14,15</sup> with Fe *d* bands near  $E_F$ , modest hybridization with As, and a similar shaped density of states with a pseudogap at an electron count of six *d* electrons as in the Fe-based oxyarsenides and FeSe.<sup>16,17</sup> The very different properties of these three compounds arise because of the different electron counts of the transition elements, which lead to different placements of the Fermi level. This provides an explanation for the ability to dope BaFe<sub>2</sub>As<sub>2</sub> with Co or Ni and obtain a coherent superconducting alloy.<sup>8</sup>

The Mn and Cr compounds, BaMn<sub>2</sub>As<sub>2</sub> and BaCr<sub>2</sub>As<sub>2</sub>, show rather different electronic structures from BaFe<sub>2</sub>As<sub>2</sub>, with strong spin dependent hybridization between the transition element *d* states and As *p* states. BaMn<sub>2</sub>As<sub>2</sub> is an antiferromagnetic semiconductor,<sup>18,19</sup> while BaCr<sub>2</sub>As<sub>2</sub> is an antiferromagnetic metal with itinerant character.<sup>20</sup> It is interesting to note that although the electronic structures and properties of the Fe compounds, FeSe and BaFe<sub>2</sub>As<sub>2</sub> are similar, the trends with transition element substitution in the ThCr<sub>2</sub>Si<sub>2</sub> structure pnictides are very different from those in the  $\alpha$ -PbO structure selenides, presumably reflecting the different chemistry of pnictogens and chalcogens.<sup>21</sup> Synthesis of BaCu<sub>2</sub>As<sub>2</sub> and SrCu<sub>2</sub>As<sub>2</sub> was reported by Pfisterer and Nagorsen,<sup>22</sup> but little is known about their electronic structure or physical properties. Here we investigate the properties of the Cu compounds BaCu<sub>2</sub>As<sub>2</sub> and SrCu<sub>2</sub>As<sub>2</sub> using density functional calculations.

The present first principles calculations were done within the local density approximation (LDA) using the general potential linearized augmented planewave

(LAPW) method,<sup>23</sup> similar to prior calculations for BaFe<sub>2</sub>As<sub>2</sub>.<sup>15</sup> We used the reported experimental lattice parameters,<sup>22</sup>  $a=4.446$  Å,  $c=10.007$  Å, for BaCu<sub>2</sub>As<sub>2</sub> and  $a=4.271$  Å,  $c=10.018$  Å, for SrCu<sub>2</sub>As<sub>2</sub>. The internal parameter,  $z_{As}$  was determined by energy minimization. The resulting values were  $z_{As}=0.3657$  for BaCu<sub>2</sub>As<sub>2</sub> and  $z_{As}=0.3697$  for SrCu<sub>2</sub>As<sub>2</sub>. We used well converged basis sets, including local orbitals to treat the semi-core states and relax the Cu *d* state linearization.<sup>24</sup> Relativistic effects were included at the scalar relativistic level. The LAPW sphere radii were 2.2  $a_0$  for Ba and Sr and 2.1  $a_0$  for Cu and As.

The calculated electronic densities of states (DOS) and band structures are shown in Figs. 1 and 2. Both BaCu<sub>2</sub>As<sub>2</sub> and SrCu<sub>2</sub>As<sub>2</sub> are metallic. As may be seen, the Cu *d* bands are narrow and are located at high binding energy, more than 3 eV below the Fermi energy,  $E_F$ . Furthermore, there is very little Cu *d* contribution to the DOS near  $E_F$ . Therefore, the Cu *d* orbitals are fully occupied in these compounds and are chemically inert. However, it is interesting to note that the Cu bands are somewhat broader in SrCu<sub>2</sub>As<sub>2</sub> than in BaCu<sub>2</sub>As<sub>2</sub>, reflecting the shorter Cu-Cu distance in the Sr compound (3.02 Å, vs. 3.14 Å). In any case, the Cu *d* bands lie on top of a background of broad pnictogen *p* and metal *sp* bands extending from -6 eV to above  $E_F$ . Therefore these compounds are *sp* metals. Turning to the band structure, which is plotted along lines either in the basal plane (constant  $k_z$ ) or along  $k_z$ , it is clearly seen that there are strong dispersions in both the *ab* plane and along the *c*-axis ( $k_z$ ) directions, showing three dimensional character.

The calculated Fermi surfaces for BaCu<sub>2</sub>As<sub>2</sub> and SrCu<sub>2</sub>As<sub>2</sub> are shown in Figs. 3 and 4, respectively. The Fermi surfaces are large and quite three dimensional. The Fermi surface of BaCu<sub>2</sub>As<sub>2</sub> shows electron pockets along the  $(1/2, 1/2, k_z)$  direction (the center of the right panel of Fig. 3, and large complex sheets around  $(0, 0, k_z)$ . In SrCu<sub>2</sub>As<sub>2</sub>, the electron pockets are larger and touch forming a large strongly corrugated electron cylinder running along the zone corner, again accompanied by complex large Fermi surfaces around the zone center.

The calculated densities of states at the Fermi energy are  $N(E_F)=1.26$  eV<sup>-1</sup> for BaCu<sub>2</sub>As<sub>2</sub> and  $N(E_F)=1.53$  eV<sup>-1</sup> for SrCu<sub>2</sub>As<sub>2</sub> on a per formula unit basis. The corresponding Fermi velocities are  $\langle v_x^2 \rangle^{1/2}=2.8 \times 10^5$

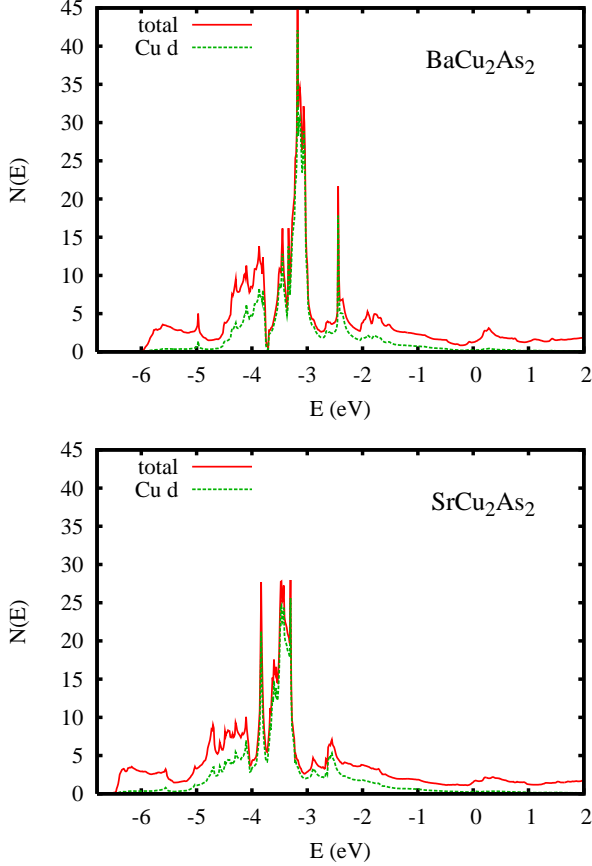


FIG. 1: (color online) Electronic density of states and Cu  $d$  projection for  $\text{BaCu}_2\text{As}_2$  (top) and  $\text{SrCu}_2\text{As}_2$  (bottom).

$m/s$  and  $\langle v_z^2 \rangle^{1/2} = 2.6 \times 10^5$  m/s for  $\text{BaCu}_2\text{As}_2$  and  $\langle v_x^2 \rangle^{1/2} = 2.8 \times 10^5$  m/s and  $\langle v_z^2 \rangle^{1/2} = 2.5 \times 10^5$  m/s for  $\text{SrCu}_2\text{As}_2$ , consistent with weakly anisotropic three dimensional transport in both compounds. The high Fermi velocities reflect the dispersive nature of the  $sp$  bands near  $E_F$ . The values of  $N(E_F)$  are high for an  $sp$  metal, but considering the extended nature of As  $p$  orbitals they are far from sufficient to yield Stoner magnetism. This was confirmed by fixed spin moment calculations of the energy as a function of constrained spin magnetization, as shown in Fig. 5. As may be seen, these compounds are not near magnetism. This is as may be expected considering the absence of  $d$  bands near the Fermi energy.

The general features of the electronic structures of  $\text{ThCr}_2\text{Si}_2$  structure pnictides have been discussed by Hoffmann and Zheng in terms of an interplay between pnictogen - pnictogen and pnictogen - metal bonding.<sup>25,26</sup> With the additional ingredient of direct metal - metal interactions, which are important in the middle of the series (Fe, Co, Ni),<sup>16</sup> this allows a classification of the compounds. According to our calculations the Cu  $d$  states are well below the Fermi energy, and therefore chemically inert in  $\text{BaCu}_2\text{As}_2$  and  $\text{SrCu}_2\text{As}_2$  and the bonding is primarily among the As atoms. In

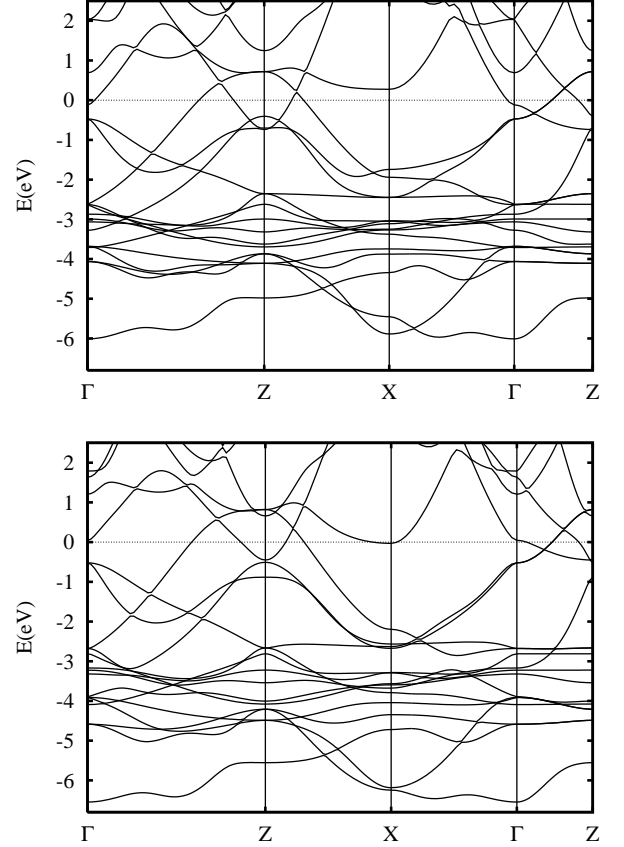


FIG. 2: Band structure of  $\text{BaCu}_2\text{As}_2$  (top) and  $\text{SrCu}_2\text{As}_2$  (bottom). The bands are plotted along lines in the basal plane and along the  $k_z$  direction. The body centered tetragonal reciprocal lattice vectors are  $(2\pi/a, 0, -2\pi/c)$ ,  $(0, 2\pi/a, -2\pi/c)$ , and  $(0, 0, 4\pi/c)$ . In terms of these, the long  $\Gamma$ -Z direction is from  $(0,0,0)$  to  $(1,0,1/2)$  in the body centered tetragonal zone, while the short  $\Gamma$ -Z direction is from  $(0,0,0)$  to  $(0,0,1/2)$ . X denotes the zone boundary  $(1/2,1/2,1/2)$  point. A two dimensional band structure would show no dispersion along the short  $\Gamma$ -Z direction and would be symmetric about the mid-point of the long  $\Gamma$ -Z direction.

the Fe, Co and Ni compounds, As is nearly anionic, and metal - metal bonding is important in addition to weaker pnictogen interactions. In the Cr and Mn compounds there is strong covalency between the metal  $d$  states and the As states, in addition to pnictogen - pnictogen covalency as evidenced by the three dimensional character of those compounds. In this regard, one may note that the  $c$ -axis lattice parameter of  $\text{BaCu}_2\text{As}_2$  is shorter by more than  $1.5$  Å, as compared to that of  $\text{BaNi}_2\text{As}_2$ . This is highly suggestive that the bonding of these two compounds is different, and in particular the shorter As - As distances in the Cu compounds reflects As - As bonding. This classification also provides an explanation for the fact that  $\text{BaFe}_2\text{Sb}_2$ ,  $\text{BaCo}_2\text{Sb}_2$  and  $\text{BaNi}_2\text{Sb}_2$  are not formed.<sup>27,28,29</sup> In particular, antimony has a greater tendency towards formation of compounds with pnictogen

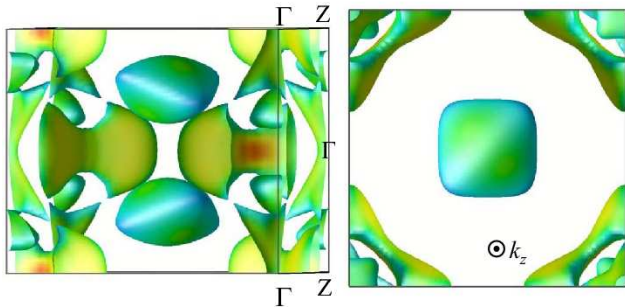


FIG. 3: (color online) Fermi surface of  $\text{BaCu}_2\text{As}_2$  shaded by velocity (light blue is low velocity). The left (right) panel shows a view perpendicular to (along) the  $c$ -axis.

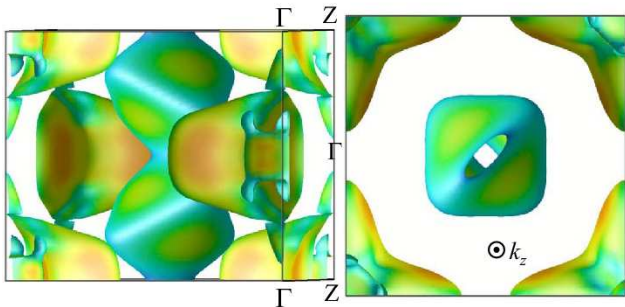


FIG. 4: (color online) Fermi surface of  $\text{SrCu}_2\text{As}_2$  shaded by velocity (light blue is low velocity). The left (right) panel shows a view perpendicular to (along) the  $c$ -axis.

- pnictogen bonding than arsenic and, as mentioned, in the Fe, Co and Ni compounds the pnictogens are anionic while metal - metal bonding is crucial.

To summarize, density functional calculations for  $\text{BaCu}_2\text{As}_2$  and  $\text{SrCu}_2\text{As}_2$  show that these materials are  $sp$  metals with dispersive bands at the Fermi energy. The Cu  $d$  bands are at high binding energy in excess of 3 eV, and are therefore inert in these compounds. These materials are not near magnetism. Therefore, the characteristic electronic structure associated with the Fe-based superconductors, in particular an electronic structure associated with anionic pnictogens and metal - metal  $d$  bonding exists in the  $\text{ThCr}_2\text{Si}_2$  structure pnictides for Fe, Co and Ni, but not Cu. The implication is that while Co and Ni can be used effectively to dope  $\text{BaFe}_2\text{As}_2$  to produce a coherent alloy with superconductivity, the other  $3d$  elements, Mn, Cr and Cu will behave differently. It

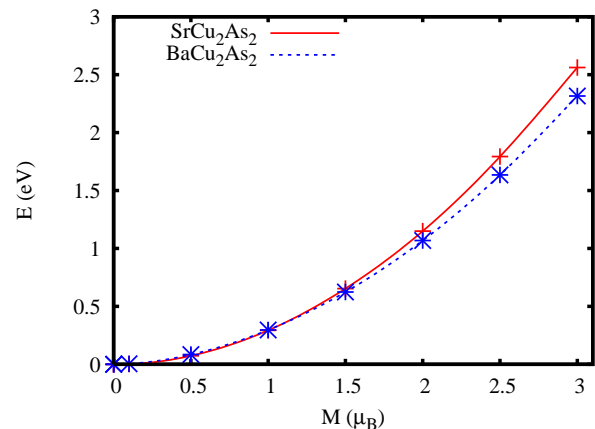


FIG. 5: (color online) Fixed spin moment energy as a function of constrained spin magnetization, shown on a per formula unit basis for  $\text{BaCu}_2\text{As}_2$  and  $\text{SrCu}_2\text{As}_2$ .

should be noted that this last conclusion does not apply to the  $\alpha$ -PbO structure chalcogenides, since the bonding and chemistry of chalcogenides are different than those of arsenides.

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